

# Electronic and crystalline structures of *zero band-gap* PdLuBi thin films grown epitaxially on MgO(100)

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Thin films of the proposed topological insulator PdLuBi - a Heusler compound with the  $C1_b$  structure - were prepared on Ta-Mo-buffered MgO(100) substrates by co-sputtering from PdBi<sub>2</sub> and Lu targets. Epitaxial growth of high-quality PdLuBi films was confirmed by X-ray spectrometry and reflection high-energy electron diffraction. The root-mean-square roughness of the films was as low as 1.45 nm, although the films were deposited at high temperature. The film composition is close to the ideal stoichiometric ratio. The valence band spectra of the PdLuBi films, observed by hard X-ray photoelectron spectroscopy, correspond perfectly to the ab-initio-calculated density of states.

**Keywords:** Heusler compounds, Thin films, Topological insulators, Electronic structure, Photoelectron spectroscopy

Zero energy consumption in electron transport, spin channel splitting, protection of spins from thermal activity, and other interesting, recently proposed, physical properties in topological insulators (TIs) would greatly improve the performance of semiconductor devices, achieve spin control in spintronics devices without application of magnetic fields, and provide an excellent platform for the application of quantum physics, e.g., quantum computers<sup>1-4</sup>. Until now, most studies of TIs have focused on HgTe/CdTe/HgTe quantum wells with two-dimensional (2D) topological states<sup>4</sup> and three-dimensional (3D) TIs, Bi<sub>1-x</sub>Sb<sub>x</sub>, Bi<sub>1-x</sub>Te<sub>x</sub>, and Sb<sub>1-x</sub>Te<sub>x</sub><sup>5-7</sup>. Electrical properties related to the quantum spin Hall effect have only been observed in HgTe/CdTe/HgTe quantum wells, which have been fabricated by molecular beam epitaxy and used as rudimentary devices. Even for HgTe/CdTe/HgTe quantum wells, the difficult and expensive fabrication of the devices has impeded further study. In order to resolve this problem, we suggest a new platform based on half-Heusler compounds for the study of TIs<sup>8</sup>. A band gap arises in half-Heusler compounds when the total number of valence electrons equals 18 as a result of a closed-shell electronic configuration<sup>9</sup>, although the material consists of three metals. The  $\Gamma_6$  and  $\Gamma_8$  bands are inverted in some semiconducting Heusler compounds with heavy elements as a result of strong spin-orbit coupling<sup>8,10</sup>. This leads to a TI state with a zero band gap that can be used in 2D TI quantum well structures. Considering the large range of lattice constants corresponding to the variety of materials and the easy fabrication conditions of Heusler com-

pounds, we suggest that TI devices with Heusler compounds may become feasible for applications. For this purpose, high-quality epitaxial PdLuBi films were fabricated by co-sputtering.

Samples with the structures MgO(100)/Mo (2 nm)/Ta (20 nm)/Mo (1 nm)/PdLuBi (40 nm)/MgO (17 nm) were prepared by direct-current magnetron co-sputtering under an Ar atmosphere. The base pressure of the sputtering chamber was below  $5 \times 10^{-7}$  Pa. The angle of inclination between each target and the substrate was about 9° and the distance between the sources and target was about 7.95 inches. The substrate was rotated during film growth. The composition of the PdLuBi thin film was analyzed by Rutherford backscattering spectrometry and particle-induced X-ray emission. The crystalline structure was examined by X-ray diffraction (D8-Discover, Bruker AXS Inc.). The surface morphologies of the films were analyzed in situ using reflection high-energy electron diffraction (RHEED, STAIB Instrument Inc.). Ex situ surface analysis was carried out using atomic force microscopy (5600LS, Agilent Technologies Inc.). The valence band spectra of the PdLuBi films were observed using hard-X-Ray photoelectron spectroscopy (HAXPES) at BL47XU of Spring-8 (Japan). For details of the HAXPES experiments, see References<sup>11-13</sup>.

Mo and Ta layers were deposited at 200°C, and then annealed at 900°C. The Mo layer was used to induce growth of Ta(100) on MgO(100) instead of Ta(110). After this process, a single-crystalline film of Ta-Mo(100) was built on MgO(100) with a 45° in-plane rotation. Because Mo and Ta can be miscible with each other at high temperatures, the lattice constant of Ta-Mo can be tuned by precise adjustment of the composition. In this study, the lattice constant of PdLuBi was slightly

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smaller than twice the lattice constant of Ta. A thin Mo layer was therefore used between the Ta and PdLuBi layers. The root-mean-square roughness of the Ta–Mo layer was below 3 Å. The PdLuBi layer was deposited at 800°C. To obtain a semiconducting Heusler film of high quality, a high substrate temperature is usually necessary. However, as a result of the low bonding energy between Bi atoms, Bi almost disappears above a substrate temperature of 600°C when the film is sputtered from three separate targets. On the other hand, the melting point of PdBi<sub>2</sub> ( $\approx 480^\circ\text{C}$ ) is much higher than that of Bi ( $\approx 271^\circ\text{C}$ ), implying a higher bonding energy of Pd–Bi. Bi was therefore sputtered from a PdBi<sub>2</sub> target to reduce the problem of Bi loss at high growth temperatures. In this case, the composition ratio of Pd:Bi could be tuned using the annealing temperature and the composition ratio of Lu:Pd could be tuned using the sputtering power. Using this procedure, films with a composition ratio of Pd:Lu:Bi = 33.5:33.4:33.1 (at%;  $\pm 1\%$ ) were obtained at 800°C.

Figure 1 shows the X-ray diffraction pattern of a PdLuBi thin film on Ta–Mo-buffered MgO(100). Only the (200) and (400) diffraction peaks of the PdLuBi film are observed in the (100) polar  $2\theta$ -scan (see 1(a)). The lattice constant of the PdLuBi film is  $\approx 6.56$  Å and corresponds to that reported for the bulk material<sup>14</sup>. The (111) polar scan and the azimuth  $\phi$ -scan of the PdLuBi(111) diffraction peak (inset of 1(b)) with four-fold symmetry prove epitaxial growth of the PdLuBi film.

The surface morphology of the film is shown in Figure 2(a). The root-mean-square roughness is around 1.45 nm, although the film was deposited at 800°C. The RHEED pattern of the PdLuBi film without a cap layer is shown in Figure 2(b). It is known that single-crystalline films with an atomically flat 2D surface produce a stripe pattern, whereas single-crystalline films with an atomically rough (3D) surface produce a transmission pattern, i.e., a set of broad spots<sup>15</sup>. Polycrystalline films and textured films without in-plane orientation form a set of concentric circles instead. It is clear from Figure 2 that a spotty pattern was observed. This indicates that a single-crystalline PdLuBi film with an atomically rough surface—either via a 3D island (Volmer–Weber) growth mode or a layer-plus-island (Stranski–Krastanov) growth mode—was obtained successfully.

The electronic structure of PdLuBi was calculated using WIEN2K<sup>16</sup>. More details are given in Reference<sup>17</sup>. Spin–orbit interactions were included for all atoms and LDA+ $U$  with the self-interaction correction double-counting scheme for Lu. An effective Coulomb energy of  $U_{eff} = U - J = 0.5$  Ry was used to reproduce the measured energy of the Lu 4*f* doublet;  $a = 6.6787$  Å was found for the relaxed lattice parameter. The result of the electronic structure calculations is shown in Figure 3. The compound turns out to be similar to a *zero* band gap semiconductor (compare<sup>18,19</sup> and references there). The optical gap at  $\Gamma$  is closed. The valence and conduction bands have a small overlap of about 130 meV. A frac-

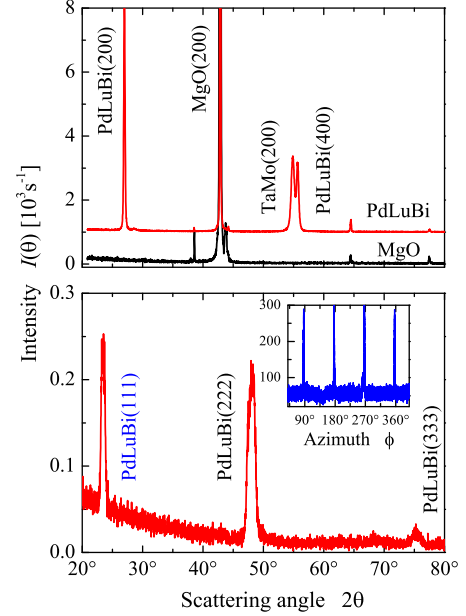


FIG. 1. (Color online) X-ray diffraction patterns of thin PdLuBi films on Ta–Mo-buffered MgO(100). (a) (100) polar scan of PdLuBi (red curve); the black solid curve indicates the background from the MgO(100) substrate. (b) (111) polar scan of PdLuBi and azimuth scan of PdLuBi(111) (inset).

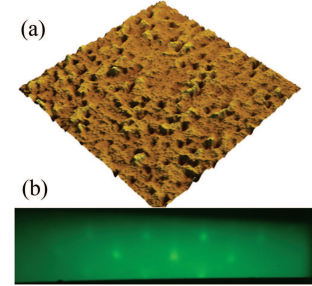


FIG. 2. (Color online) Morphology of thin PdLuBi films. (a) Atomic force microscopy three-dimensional surface representation of PdLuBi with cap layer, (b) reflection high-energy electron diffraction pattern of PdLuBi.

tion of about  $10^{-3}$  electrons is found in the conduction band. This situation may change for slightly smaller lattice parameters (see Figure 3(c)) or a slight tetragonal distortion. Both effects are principally able to open up the band gap again at  $\Gamma$  (compare also Reference<sup>10</sup>). A slight tetragonal distortion may particularly occur in thin films with pseudomorphic growth.

Valence band spectra of PdLuBi are presented in Figure 4 and compared to the calculated density of states. Figure 4(a) shows the valence band spectra excited by photons of energy about 8 keV. The high intensity with a maximum between -12.5 and -11 eV corresponds to excitation of the low-lying Bi *s* states with  $a_1$  symmetry,

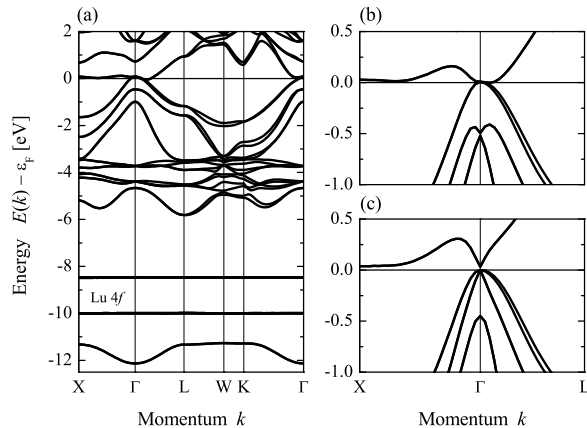


FIG. 3. Electronic structure of PdLuBi.

(a) shows the complete band structure for the relaxed lattice parameter. (b) and (c) show the band structure in the vicinity of the Fermi energy for the thin film lattice parameter and a 5% compressed lattice parameter, respectively. In (c), a small band gap of width 40 meV is opened. Calculations were performed with spin-orbit interactions for all elements and LDA+ $U$  for the Lu 4f electrons.

as is seen by comparison with the density of states. The Lu  $4f_{5/2}$ - $4f_{7/2}$  spin-orbit doublet is found at energies of  $E_{5/2} = -9.76$  eV and  $E_{7/2} = -8.31$  eV, with a spin-orbit splitting of  $\Delta_{SO} = 1.45$  eV. The Lu 4f states reside on top of the states from the MgO protective overlayer that usually appear at about -9 eV. Such MgO states were previously also observed in the spectra from MgO-covered  $\text{Co}_2\text{MnSi}^{11}$ . The upper part of the valence spectra above -6.5 eV exhibits the typical structure of the PdLuBi valence  $d$  bands with four major maxima (-6, -5.16, -4.31, -2.1 eV) and a smaller one at -2.9 eV. The splitting of the states at about -4 eV is not resolved in the spectrum. Slight energy differences between the maxima in the density of states and maxima of the spectrum are observed. These energy shifts are larger for states further away from the Fermi energy (for example 0.3 eV at the -2.1 eV maximum and 0.6 eV at the -5.16 eV maximum). This is a typical effect of the photoemission process and emerges from the complex self-energy of the photoelectrons interacting with the remaining  $N - 1$  electron system. The spectra exhibit no clear cut-off at the Fermi energy as is observed when a metallic-type density is terminated by the Fermi-Dirac distribution, but a rather smooth, linearly decreasing intensity is observed. A similar behavior was found in bulk materials of the *zero* band gap Heusler compounds  $\text{PtYSb}^{18}$  and  $\text{PtLuSb}^{19}$ . A splitting of the La  $3d$  states was reported for thin  $\text{PtLaBi}$  films grown on  $\text{YAlO}_3(001)$  by three-source magnetron co-sputtering<sup>20</sup>. The appearance of the satellite peaks is explained as being the result of charge transfer, as appears, for example, in oxides. The PdLuBi films reported here did not exhibit any additional splitting of core levels, which also indicates their high quality with respect to impurities,

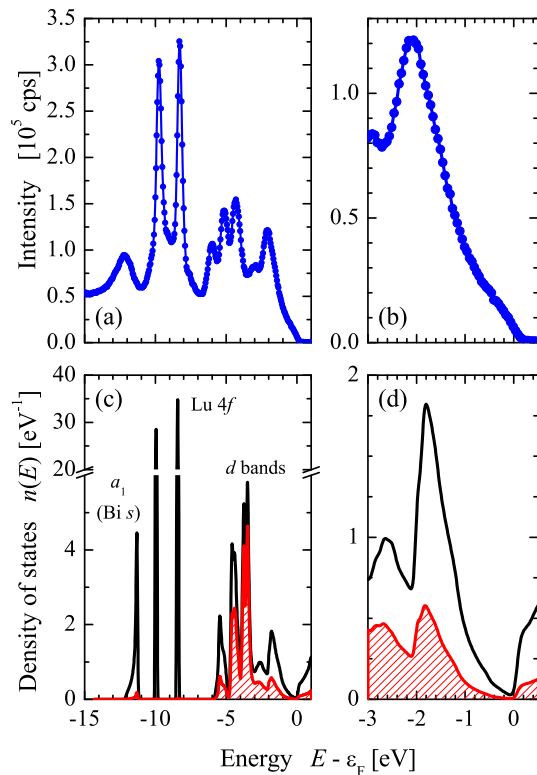


FIG. 4. (Color Online) Valence band of PdLuBi.

(a)–(b) show the valence band spectra taken with a photon energy of about 8 keV. (c)–(d) show the density of states, and the density localized at the Pd atoms is marked by the shaded area. (b) and (d) show the valence band close to the Fermi energy on an enlarged scale.

structure, and composition.

In summary, high-quality epitaxial thin films of the Heusler TI PdLuBi were successfully prepared. The composition of Pd:Lu:Bi in the film grown at 800°C is stoichiometric, with ratios of 1:1:1. The valence band spectra of thin PdLuBi films observed by HAXPES perfectly match the density of states from first principles calculations. PdLuBi has a similar band structure to that of HgTe and thus may be used for the construction of 2D TI quantum well structures.

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